Formation of a Novel η3

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Table I. Specific Rate per Meter Squared of Surface Area of Maleic Anhydride Formation from *n*-Butane, Specific Rate of *n*-Butane Depletion, and Specific Rate of But-1-ene Depletion on the Catalysts (a) and (b)[a]

catalyst	temp, K	*n*-butane oxidn		but-1-ene oxidn
		$r_{\text{maleic anhydride}}$, mol s^{-1} m^{-2}	$-r_{n\text{-butane}}$, mol s^{-1} m^{-2}	$-r_{\text{but-1-ene}}$, mol s^{-1} m^{-2}
(a)	560			0.88×10^{-9}
(a)	620			0.81×10^{-8}
(a)	660	0.29×10^{-9}	0.58×10^{-9}	
(a)	690	1.02×10^{-9}	2.68×10^{-9}	
(b)	560			1.03×10^{-9}
(b)	620			0.92×10^{-8}
(b)	570	1.58×10^{-9}	1.95×10^{-9}	
(b)	600	2.58×10^{-9}	3.79×10^{-9}	

[a] Experimental conditions: reagent composition, 0.5% hydrocarbon, 12.6% oxygen, 86.9% nitrogen, conversion lower than 10%; 1 g of catalyst.

be attributed to ν_{CN} of coordinatively bonded acetonitrie on very strong Lewis sites.

In conclusion, the acetonitrile adsorption on the two catalysts suggests the following surface properties: (i) both medium-strong and very strong Lewis sites are present on the $(VO)_2P_2O_7$ surface and (ii) a much higher concentration of very strong Lewis sites is present in the catalyst prepared in an organic medium [(b)] as compared to the catalyst prepared in an aqueous medium [(a)].

The catalytic properties of these two catalysts in *n*-butane and but-1-ene selective oxidation to maleic anhydride are reported in Table I. Catalyst (b) is much more active in *n*-butane-selective oxidation than catalyst (a), whereas no significant differences are found in but-1-ene oxidation.

It has been shown that the first step in the conversion of *n*-butane on solid super acid[14] is the extraction of an H^- from the butane by very strong Lewis sites. Similarly it is possible to hypothesize that the very strong Lewis sites evidenced on catalyst (b) and to a lesser extent on catalyst (a) are the sites responsible for the first step in alkane activation. The presence on the vanadium–phosphorus oxides of an oxidizing function (V=O double bond) together with the strong Lewis sites modifies the successive steps of the reaction and leads to selective products (maleic anhydride) instead of the isomerization or cracking products which occur on solid super acid.[14]

The presence of medium-strong Lewis sites is related to the structure itself of the $(VO)_2P_2O_7$[9] and it is not usual on vanadium oxides. Our FT-IR studies of the adsorption of bases indicate that such sites are not present on V_2O_5 even after reducing treatments. On the predominantly exposed (020) plane of $(VO_2)_2P_2O_7$,[9,10,15-17] coupled vanadyl ions in trans positions leave coordinatively unsaturated V(IV) ions that, due to the higher electronegativity of the neighboring phosphorus atoms, give rise to a medium-strong Lewis site. Accordingly, the quantitative determination by temperature-programmed desorption[18] of the presence of medium-strong Lewis sites indicates that their concentration is fairly independent of the preparation method and depends only on the surface area, just as in the case for the oxidation of but-1-ene. The presence of very strong Lewis sites, on the contrary, would be due to defective crystal states, their concentration depending on the preparation method, as shown in Figure 1.

During the $VOHPO_4 \cdot {}^1/_2H_2O$ precursor preparation in an organic medium, alcohol remains trapped between the layers.[9] During successive calcination to form $(VO)_2P_2O_7$ the presence of the alcohol provokes local deformation[9] of the crystalline structure as shown by X-ray diffraction analysis, thus inducing local straining of the V-(O-P) bonds. As a result, the coordination requirements of the vanadium are not completely satisfied, with the consequent enhancement of the Lewis acid strength and creation of new very active sites able to activate the paraffins.

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Registry No. $(VO)_2P_2O_7$, 58834-75-6; *n*-butane, 106-97-8; but-1-ene, 106-98-9; acetonitrile, 75-05-8.

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Formation of a Novel η^3:η^4-1,2,3-Trimethyl-4,5-dimethylenecyclopentenyl Ligand by Hydrogen Abstraction from a Permethylcyclopentadienyl Group in Permethyltitanocene Carbyl and Related Systems

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We wish to report a new type of transformation of a pentamethylcyclopentadienyl group (Cp*) by stepwise hydrogen abstraction into an η^3:η^4-1,2,3-trimethyl-4,5-dimethylenecyclopentenyl ligand.

The reaction was observed during a study of the thermolysis of paramagnetic titanium(III) compounds Cp^*_2TiR (I).[1] A stepwise reaction was observed, with the stoichiometry[2] given in eq 1.

$$\underset{\text{I}}{Cp^*_2TiR} \xrightarrow{-RH} \underset{\text{II}}{Cp^*(C_5Me_4CH_2)Ti} \xrightarrow{-{}^1/_2H_2} \underset{\text{III}}{Cp^*(C_5Me_3(CH_2)_2)Ti} \quad (1)$$

R = Me, Et, Pr

Hydrogen abstraction from a transition-metal-bonded Cp* ligand with formation of a 1,2,3,4-tetramethylfulvene metal complex has been observed before[3,4] and in fact II was reported as a product of the thermal decomposition of Cp^*_2Ti.[5] Similar reactivity of the Cp* functionality is suggested for group 3 and 4f element compounds Cp^*_2MR (M = Sc,[6] Lu[7]), where intermediates like II are of crucial importance to explain the rapid C-H activation of these systems.

When we studied the thermal decomposition of I, quantitative formation of RH and II[8] was observed. Prolonged heating of paramagnetic II at 150 °C resulted in the formation of H_2 and

(1) Hissink, C. E.; Luinstra, G. A.; Pattiasina, J. W.; Teuben, J. H., unpublished results.
(2) (a) The stochiometry was confirmed by isolation of the titanium compounds and Toepler pump determination of the gaseous products. (b) Thermolysis of I was carried out with 10.0 g (30 mmol) of Cp^*_2TiMe in 25 mL of toluene at 110 °C. In 12 h the color of the solution had changed from green to purple. The solvent was stripped and the product crystallized from ether. Yield 7.5 g (9.3 mmol, 75%) of II.
(3) (a) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219-1238. (b) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629-1634.
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(8) Identical with the compound in ref 5, on basis of elemental analyses (C, H, Ti), mass spectrum, molecular weight (cryoscopically determined in benzene), IR, and ^1H NMR.

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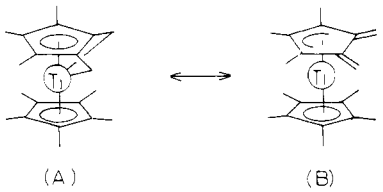

(A) (B)

Figure 1. Modes of bonding in $Cp^*(C_5Me_3(CH_2)_2Ti$.

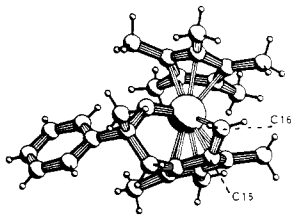

Figure 2. Molecular structure of $Cp^*TiC_5Me_3(CH_2)CH_2CO(Me)(Ph)$.

a blue, diamagnetic organotitanium compound III.[9] The elemental analyses, molecular weight (cryoscopy in benzene), mass spectrum, IR spectrum, but especially ^1H and ^{13}C NMR data are in complete accordance with a formulation as a monomeric $(\eta^5\text{-}Cp^*)(\eta^3{:}\eta^4\text{-}C_5Me_3(CH_2)_2)Ti$ complex with a unique 1,2,3-trimethyl-4,5-dimethylenecyclopentenyl ligand. The bonding in this compound is very intriguing, given the possibility of two resonance structures (Figure 1).

The main difference is the formal oxidation state of the metal, which varies from +4 in A to +2 in B. Structure A is an analogue of regular $Cp^*_2TiR_2$ with two Ti–C σ bonds to the cyclopentadienyl methylene groups. In structure B the trimethyldimethylenecyclopentenyl ligand is in an η^3-allyl-η^4-butadiene bonding fashion and in this sense analogous to complexes of the type Cp^*M(1-methallyl)(butadiene) (M = Ti, Zr, Hf).[10]

NMR data indicate that structure B is the best representation. The coupling constants for both methylene groups ($^2J_{HH}$ = 4.4 Hz and $^1J_{CH}$ = 160 Hz) are typical for sp^2 hybridized carbon atoms, thus favoring B.

An X-ray structure determination of III to verify both relative position and the bonding situation of the methylene groups is hampered by disorder problems. Conformation of the proposed structure comes from the molecular structure of the acetophenone reaction product IV of III[11] (Figure 2). The acetophenone carbonyl function is inserted in a titanium methylene bond, forming an alkoxide bridging titanium and a (substituted) 1,2,3,4-tetramethylfulvene ligand. Compound IV is the first structurally characterized monomeric titanium fulvene complex. Relevant for the structure of III is the fact that the two methylene functions are indeed on neighboring ring C-atoms, thus confirming the 1,2,3-trimethyl-4,5-dimethylenecyclopentenyl structure proposed for III. The bonding of the fulvene methylene group is very interesting. The short C=CH_2 bond (1.437 (5) Å), the angle HC(16)H (116 (3)°), and the rather small deviation of the CH_2 hydrogen atoms from a planar array with C(15) and C(16) (the angle between C(15)–C(16) and the plane HC(16)H is 27.8 (2)°) indicate that in first approximation we are dealing with an sp^2 hybridized methylene carbon atom. The coupling constants ($^2J_{HH}$ = 3.6 Hz and $^1J_{CH}$ = 150 Hz) are in agreement with this view. However, the deviation of the C=CH_2 fragment from the ring plane (36.3°) indicates an η^2-bonding of this olefinic function to the metal. Comparison with a real titanium olefin complex $Cp^*_2TiC_2H_4$[12] reveals indeed a strong similarity. The C–Ti–C angle (37.8 (1)° in IV and 38.9 (1)° in $Cp^*_2TiC_2H_4$ is virtually the same in both compounds. The Ti–C distances, however, (Ti–C(15) = 2.317 (3), Ti–C(16) = 2.281 (3) Å against 2.160 (4) Å in $Cp^*_2TiC_2H_4$) differ considerably.

In conclusion we may state that both molecular structure and NMR data for IV favor bonding structure B for III, containing a so far unknown bifunctional, e.g., an η^3-allyl, η^4-diene organic ligand.

Compound III is not accessible through II only. Thermal decomposition of $Cp^*_2TiMe_2$ is known to undergo hydrogen abstraction from a Cp^* ligand giving $Cp^*(C_5Me_4CH_2)TiMe$.[3] We observed that heating of the latter compound in mesitylene at 160 °C also produces III (obtained yield 22%) (eq 2).

$$Cp^*_2TiMe_2 \xrightarrow{-MeH} Cp^*(C_5Me_4CH_2)TiMe \xrightarrow{-MeH} \underset{\text{III}}{Cp^*(C_5Me_3(CH_2)_2)Ti} \quad (2)$$

This stepwise hydrogen abstraction from Cp^* ligands is not limited to titanium. The group 4 homologue $Cp^*_2ZrMe_2$[13] gives the same reaction. $Cp^*(C_5Me_3(CH_2)_2)Zr$ could be isolated in 4% yield as a red crystalline material after heating $Cp^*_2ZrMe_2$ at 160 °C in mesitylene.[14]

We are at the moment investigating the reactivity of the new $\eta^3{:}\eta^4$-1,2,3-trimethyl-4,5-dimethylenecyclopentenyl ligand and the scope of the stepwise hydrogen abstraction from Cp^* ligands in metal carbyls.

Note Added in Proof: Recently, observations similar to ours have been reported for the tungsten system $Cp^*_2WH_2$, which under irradiation produces tungsten analogues of II and III.[15]

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Supplementary Material Available: Details of the synthesis of and analytical data for I, thermal decomposition of I, thermolysis of $Cp^*_2MMe_2$ (M = Ti, Zr), and synthesis of IV and tables of fractional atomic coordinates, thermal parameters, bond distances, and structure of IV (10 pages). Ordering information is given on any current masthead page.

(9) 4.0 g (12.5 mmol) of II was heated to 150 °C for 120 h in 15 mL of *o*-xylene. The solvent was stripped and the product crystallized from pentane. Yield 2.8 g (9.3 mmol, 75%) of III. Anal. Calcd for $C_{20}H_{28}Ti$: C, 75.93; H, 8.92; Ti, 15.14. Found: C, 75.79; H, 8.89; Ti, 15.03. IR (KBr/Nujol) 3020, 2710, 1480, 1365, 1335, 1160, 1070, 1020, 872, 830, 810, 800, 725, 660, 620, 580, 550, 445, 410 cm^{-1}; ^1H (200.068 MHz) and ^{13}C (50.31 MHz) NMR in C_6D_6; ^1H (ppm relative to residual protons in deuterated solvent at δ 7.15) δ 1.79 (s, 15, Cp*), 1.34 (s, 3, Me), 1.14 (s, 6, 2 Me), 0.92, 0.86 (d, d, 2, 2, $^2J_{HH}$ = 4.4 Hz, 2 CH_2); ^{13}C data (ppm relative to C_6D_6 at δ 127.96) δ 144.60, 133.18, 122.70 (all s, $C_5Me_3(CH_2)_2$), 119.06 (s, C_5Me_5), 67.64 (t, $^1J_{CH}$ = 160 Hz, $C_5Me_3(CH_2)_2$), 11.79 (q, $^1J_{CH}$ = 125 Hz, C_5Me_5), 10.13, 9.98 (both q, $^1J_{CH}$ = 125 Hz, $C_5Me_3(CH_2)_2$); MS, parent peak at *m/e* 316. Cryoscopic molecular weight determination in C_6H_6: calcd 316; found 332.

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(11) Acetophenone reacts with III in pentane (reaction time 24 h at 22 °C) according to

$$III + PhCOMe \rightarrow \underset{\text{IV (60\%)}}{Cp^*TiC_5Me_3(CH_2)CH_2CO(Me)(Ph)}$$

Compound IV was identified by elemental analyses (C, H, Ti), mass spectrum, IR, and ^1H and ^{13}C NMR. Suitable crystals of IV were grown from a pentane solution. The structure of IV was determined by X-ray crystallography. Crystal data: $C_{28}H_{36}OTi$, M_r = 436.5; monoclinic, $P2_1/c$; Z = 4; a = 15.969 (3) Å, b = 9.721 (2) Å, c = 16.193 (2) Å; β = 112.75 (1)°; R = 0.043, R_w = 0.040 ($\omega = 1/\sigma^2(F)$); based on 2715 reflections with $I > 2.5\sigma(I)$ out of 4076 unique CAD4 diffractometer data. Hydrogen atoms, located from a difference electron density map, were refined isotropically all other atoms anisotropically. Full details will be published elswhere.

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(14) IR (KBr/Nujol) 3020, 2720, 1480, 1375, 1340, 1070, 1020, 855, 825, 800, 705, 550, 405 cm^{-1}; ^1H (200.068 MHz) and ^{13}C (50.31 MHz) NMR in C_6D_6; ^1H data (ppm relative to Me_4Si at δ 0.00) δ 1.93 (s, 15, Cp*), 1.46 (s, 3, Me), 1.27 (s, 6, 2 Me), 0.97, 1.17 (d, d, 2, 2, $^2J_{HH}$ = 6.2 Hz, 2 CH_2); ^{13}C data (ppm relative to C_6D_6 at δ 127.96) δ 137.12, 131.51, 128.25 (all s, $C_5Me_3(CH_2)_2$), 119.48 (s, C_5Me_5), 56.52 (t, $^1J_{CH}$ = 148 Hz, $C_5Me_3(CH_2)_2$), 11.51 (q, $^1J_{CH}$ = 126 Hz, C_5Me_5), 10.96, 10.45 (both q, $^1J_{CH}$ = 126 Hz, $C_5Me_3(CH_2)_2$).

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